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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Terpenes and their oxidation products in the French Landes forest: insight from Vocus PTR-TOF measurements" *by* Haiyan Li et al.

Anonymous Referee #1

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The paper describes the results of organic trace gas measurements by Vocus PTR-TOF in the French Landes forest in the summer of 2018. The Vocus PTR-TOF is a newly developed PTR-MS instrument with improved detection limits and mass resolution, and the paper highlights the large number of compounds that can be detected with this instrument. In addition to the more commonly measured monoterpenes, the paper presents measurements of sesquiterpenes and diterpenes. The paper also illustrates that many oxidation products of these hydrocarbon precursors are detected. The analysis of the data is rather descriptive and focuses on diurnal variations and the potential importance of different oxidants in forming the observed products. Overall, the paper is suitable for publication in Atmospheric Chemistry and Physics after incorporation of

the comments below.

Section 2: A better description of the site is needed. Specifically, VOCs are sampled at 2 m height, which is well inside the canopy. How high are the treetops in this forest and how open is the canopy? Several studies have shown how strongly the mixing ratios of monoterpenes, light-dependent VOCs like MBO and their oxidation products can depend on height within the canopy (Holzinger et al., 2005). Some more discussion of the results in this context would be good to add to the paper.

Lines 38-40: The atmospheric chemistry of BVOCs has been studied much longer than just the past few years (Kanakidou et al., 2005). In general, the paper could do a better job citing the relevant literature. Much was learned about isoprene and monoterpene chemistry before the recent introduction of TOF-CIMS instruments.

Line 49: "irreversibly" instead of "irremediably".

Lines 54-56: The lack of sesquiterpene measurements by PTR-MS are mostly due to a lack of sensitivity.

Lack 60-62: I recommend adding a quantitative indication rather than "drastically enhanced" to describe how the sensitivities compare with other instruments.

Lines 97-99: I recommend adding the exact operating pressure in the reactor instead of a range. The difference between 1.0 and 1.5 mbar corresponds to a very large difference in E/N and therefore cluster ion distributions, fragmentation, etc.

Line 106: Have you considered how the use of nitrogen instead of zero air affects the ion chemistry and therefore background ion signals in the instrument?

Lines 117-118: This was not quite clear. Did your calibration mixture contain all three monoterpenes at 70 ppbv? In that case, your measured sensitivity is an average for the three monoterpenes. It is also not clear how you can use this average to determine the sensitivity as a function of reaction rate coefficient.

Lines 117-118: The lack of calibration for an oxygenated compound is a concern. The distribution of H3O+ and H3O+(H2O) reagent ions affects the sensitivity for hydrocarbons and polar molecules differently, but the distribution is difficult to determine in a Vocus PTR-TOF as H3O+ ions are very poorly detected. As the exact quantification of oxidation products is not a major focus in this study, I do not think it is a problem, but moving forward the Authors should consider calibrating their instrument for a much wider range in compounds.

Lines 120-122: I think this relationship needs to be included graphically. It seems that the range in rate coefficients is small and the resulting uncertainty in the factor 509.75 would consequently be very large.

Lines 123-125: It is trivial to determine the fragmentation of the monoterpenes in your calibration mixture and correct your measured sensitivities for fragmentation. This could be a large correction, so more detail needs to be given here.

Line 147: I do not think that inlet memory effects necessarily lead to an overestimate of sensitivities in this work. It all depends on how the passivation time of the inlet relates to the timescale of atmospheric variability. Memory effects can both lead to an underestimate and overestimate of measured mixing ratios.

Lines 163-164: It would take a lot of monoterpenes to consume 50 ppbv of ozone. Some back of the envelope estimate may be useful to constrain the chemical sink of ozone. Surface uptake is likely another important sink of ozone in the canopy.

Lines 177-179: Use “exact mass” instead of “accurate mass”.

Lines 187-187: C6-C9 hydrocarbons are also notable. Some of these can be fragments of monoterpenes and sesquiterpenes. Also, the mass cut-off by the BSQ affects what can be seen below m/z $\sim$40 and the readers need to be made aware of that.

Lines 191-194: Biogenic butene is not very likely the cause for the elevated C4H9+ signal. As discussed, butanol is a more likely explanation. In addition, ions like C3H7+

and C4H9+ are very common fragments from many VOCs and are often prominent in the mass spectra (Pagonis et al., 2019).

Lines 215-216: Add the difference between UTC and local time. Given the diurnal variations in Fig. 4, the definition of day- and nighttime data seems a bit off.

Lines 224-235: I think the attribution of C5H9+ ions to isoprene should be considered in more detail. Isoprene mixing ratios are not very high in this study, and other VOCs are also detected at this mass. Notably, do the tree species at this site release MBO (Holzinger et al., 2005)?

Lines 268-274: Some further explanation of how the authors think monoterpenes could be detected as C15 and C20 is needed here.

Lines 290-292: The instrument settings used can indeed be the main explanation here and should be included in this paper.

Lines 315-317: Methyl vinyl ketone and methacrolein are the most common products from isoprene reactions with OH. The observation of C4 products does not necessarily imply ozone reactions.

Lines 327-337: This back-of-the-envelope analysis can be easily extended with estimates of the OH formation rate from alkene + ozone reactions, and the OH concentration in steady state. AN OH concentration of 10,000 seems very low.

Figure 2: Some indication of the low mass cut-off is needed to fully appreciate this graph: the Vocus PTR-TOF is less sensitive below m/z $\sim$40 depending on the BSQ settings and many readers will not fully understand that. The colors used in panel b for day and night are hard to distinguish for the color blind. In the caption, use “exact mass” instead of “accurate mass”.

References

Holzinger, R., Lee, A., Paw, K. T. and Goldstein, A. H.: Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds, Atmos. Chem. Phys., 5, 67–75, 2005.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y. J., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G. and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053–1123., 2005.

Pagonis, D., Sekimoto, K. and de Gouw, J. A.: A library of proton-transfer reactions of H3O+ ions used for trace gas detection, J. Am. Soc. Mass Spectrom., 30, 1330–1335, doi:10.1007/s13361-019-02209-3, 2019.

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